

The electronic structures and magnetic properties of perovskite ruthenates from constrained orbital hybridization calculations

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We introduce a method to analyze the effect of hybridization by shifting corresponding atomic levels using external potentials. Based on this approach, we study perovskite ruthenates, and unambiguously identify that the covalency between the *A*-site cation and O ion will modify the Ru-O hybridization and change the density of state at Fermi level, consequently affect the magnetic properties significantly. We also study the effect of pressure and reveal that hydrostatic pressure has a small effect on the Ru-O-Ru bond angle of SrRuO₃, while it will decrease the Ru-O length and increase the band width significantly. Therefore, the magnetic ordering temperature will decrease monotonically with pressure.

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Due to the interesting electrical, structural and magnetic properties, perovskite ruthenates have attracted continual research attention[1–19]. SrRuO₃ crystallizes in an orthorhombic structure with space group *Pbnm*[2]. Same as SrRuO₃, CaRuO₃ also has an GdFeO₃-type perovskite structure[2], the only observable difference between their crystal structures is the Ru-O-Ru bond angle. However, their magnetic properties are different completely. SrRuO₃ is a ferromagnetic (FM) metal with a Curie temperature $T_c=160$ K[4], while there is a debate about the ground state of CaRuO₃[1, 5, 18, 19]. It is believed that the leading factor to determine the magnetic properties of these 4*d* materials is the structural distortion and the associated Ru-O-Ru bond angle[20]. Comparing with Sr²⁺, Ca²⁺ has smaller radii, therefore CaRuO₃ has bigger structural distortion and smaller Ru-O-Ru bond angle, which lifts the band degeneracy and reduces the density of states at the Fermi energy $N(E_f)$ [20]. Consequently the Stoner criterion for magnetism may not be satisfied for CaRuO₃. On the other hand, Ba²⁺ has bigger radii, so perovskite BaRuO₃ will have larger Ru-O-Ru bond angle, comparing with that of SrRuO₃. Thus it is very natural to expect that BaRuO₃ should have higher T_c than SrRuO₃.

Very recently, using high pressure and high temperature techniques, Jin *et al.*[21], synthesize the cubic perovskite BaRuO₃ successfully. The Ru-O-Ru bond angle of cubic BaRuO₃ is 180°, which is indeed larger than that of SrRuO₃. However, its T_c is only 80 K, which clearly indicates that in addition to the bond angle, there is other factors which also play important roles in the magnetic properties. Jin *et al.*[21] propose that the weaker Ba-O hybridization will enhance the strength of Ru-O bond, consequently reduce the T_c . The importance of *A*-site cation has also been emphasized by the density function calculations [22–24]. However contrast to Jin[21], Zayak *et al.*[24] suggest that the magnetization in these compounds is anticorrelated with the degree of covalency

between *A*-site ion and O ion.

In addition to Ru-O-Ru bond angle and *A*-site hybridization, Ru-O bond length is another factor which also affect the band structure and the $N(E_f)$, consequently change the magnetic properties. Hydrostatic pressure may vary both the bond length and angle, and there are several publications which study the effect of pressure[25–28]. All experiments indicate that the T_c of SrRuO₃ will decrease with pressure[25–28]. However, the reason why T_c decreases with pressure is still not clear. X-ray diffraction[27] suggests the Ru-O-Ru bond angle will decrease with pressure, which results in the decrease of T_c . On the other hand, neutron powder diffraction[28] claims that the Ru-O bond length is sensitive to pressure while the bond angle remains almost constant. Therefore, to clarify the controversial issue about the influence of *A*-O covalence and pressure on the magnetic properties of perovskite ruthenates is an interesting problem which we address in the present work.

Local spin density approximation (LSDA) is well used for perovskite ruthenates[3, 9, 20, 23, 24, 29]. The main aim of our study is to illustrate the effect *A*-O hybridization, we thus neglect the effect of Coulomb correlation, although there is a debate about whether the electronic correlation is important in perovskite ruthenates[4, 19, 29, 31]. We perform the electronic band-structure calculations within LSDA using the full potential linearized-muffin-tin-orbital LMTO method[30]. A mesh of 256 *k*-points in the irreducible Brillouin Zone is used. The self-consistent calculations are considered to be converged when the difference in the total energy of the crystal do not exceed 0.25 meV per formula unit (f.u.) and the difference in the total electronic charge do not exceed 10^{-3} electronic charge at consecutive steps.

Based on the experimental structure[21], we perform calculation for the recently synthesized cubic BaRuO₃. We find that the FM metallic solution is the ground state, which agrees with the experiment[21]. The en-

ergy difference (E_{PM-FM}) between total energy of its PM and FM solution is 25.6 meV/f.u. The magnetic moment at Ru site (M_{Ru}) of BaRuO₃ is about $0.76 \mu_B$, which is also close to the experimental value (about $0.80 \mu_B$)[21]. Due to the strongly hybridization with the Ru 4*d* state, there is considerable moment locating at O site. We also perform calculation for SrRuO₃ and CaRuO₃ using their experimental structure[2]. Consistent with the experimental and previous theoretical work, our calculation also predict the ground state of SrRuO₃ is FM metal. The obtained E_{PM-FM} is 38.9 meV/f.u., which is slightly larger than that of BaRuO₃. The magnetic moment mainly locates at Ru site (about $0.93 \mu_B$), which is also in good agreement with the previous works[20]. On the other hand, for CaRuO₃, the FM state is unstable in energy, which is consistent with other theoretical work[20].

After reproducing the experimental results, we now try to explore the controversy about the effect of A-O covalence. It is widely accepted that the alkali elements at the A-site of ABO₃ perovskite are highly ionic, A-site only contribute to the distortion of lattice structure and should not affect the Ru-O hybridization considerably. However, recently the effect of hybridization between A-site cation and O had been emphasized by several groups[21–24], although there is debate about its exact effect. Thus to gain a conclusive comment about the effect of A-O hybridization is important.

It is well known that the strength of hybridization between two orbits is strongly depend on their energy difference. We thus introduce a external potential in the Kohn-Sham equation to shift the orbital level consequently control the hybridization:

$$(H_{KS} + |ilm\sigma\rangle V_{ext} \langle ilm\sigma|)\psi = E\psi$$

where, H_{KS} is the Kohn-Sham potential, the basis $|ilm\sigma\rangle$ is the orbit which we try to shift (i denotes the site, n the main quantum number, l the orbital quantum number, m the magnetic quantum number and σ the spin index), and V_{ext} is the magnitude we shift. By this constrained calculation, we can directly study how various orbitals and hybridizations between them affect the physical properties of solids. Although similar in spirit, this constrained orbital-hybridization method is different with the constrained LSDA calculation where the external potential is applied to a particular orbital to constrain the orbital occupation.

For perovskite ruthenates, the bands near the Fermi energy (E_f), which determine the magnetic properties, are mainly contributed by Ru 4*d* and O 2*p*, on the other hand the *d* band of alkali elements are several eV above E_f . Thus when we upshift the empty band of A-site atom by a external potential, the effective hybridization between this band and the O 2*p* band will decrease, therefore we can study the effect of A-O hybridization directly by our constrained orbital-hybridization method.

Based on the experimental crystal structure[2, 21], we perform constrained orbital-hybridization calculation, the numerical results reveal that the position of Sr 4*d* band affects not only the magnetic moment but also the magnetization energy E_{PM-FM} . Upshifting Sr 4*d* band by 9 eV and 20 eV will reduce M_{Ru} and E_{PM-FM} to $1.10 \mu_B$, 20.2 meV; and $0.4 \mu_B$, 7.5 meV, respectively. These results indicate the strength of Sr-O hybridization is correlated with the magnetization. Our constrained orbital-hybridization calculations also show that upshifting Ba 5*d* band has a similar effect as in SrRuO₃. The position of Ca 3*d* will also affect the band structure of CaRuO₃, but shifting Ca 3*d* band cannot make the FM state stable.

To further understand the effect of the A-O hybridization on magnetic properties, we perform constrained orbital-hybridization calculation for PM state and shows the density of states (DOS) of BaRuO₃ in Fig.1. It is found that the energy position of Ba 5*d* band has an important effect on its electronic band structure. Conventional LSDA calculation predicts that the e_g band of Ru mainly locates at -7.6 to -5.0 eV and -0.2 to 5.1 eV, while t_{2g} band has two sharp peaks centered at -0.1 and -5.2 eV, respectively, as shown in Fig.1(a). Upshifting Ba 5*d* band depresses the hybridization between Ba and O, consequently varies the band structure around E_f considerably. As shown in Fig.1(b), decreasing the Ba-O hybridization will widen the e_g band of Ru slightly, while change the t_{2g} band significantly, make the t_{2g} to distribute in the whole range from -7.0 to 0.9 eV, and decrease $N(E_f)$ considerably. It is well accepted that ARuO₃ is an itinerant magnetism, and a large $N(E_f)$ in PM calculation is crucial for the magnetization. Therefore, according to the Stoner theory, the A-O hybridization can affect the magnetic properties considerably. We also perform constrained orbital-hybridization calculation for SrRuO₃ and CaRuO₃. The similar sensitivity of electronic structure to energy position of *d* band of cation has also been found. So we can conclude that the A-O hybridization will change the Ru-O hybridization, consequently change the magnetization of perovskite ruthenates.

To study the effect of pressure on the structure, we optimize the structure and relax all independent internal atomic coordinates until the corresponding forces are less than 1 mRy/a.u. Consistent with the recent experiment[28], we find that the Ru-O-Ru bond angle of SrRuO₃ is not sensitive to the external pressure, while the Ru-O bond length decreases monotonically with pressure, as shown in Fig.2. Our numerical results agree with the experimental value at low pressures, as shown in the inset of Fig.2, while the experimental bond length at high pressure is not available. Based on the optimized structure, we perform the band-structure calculation for a number of different volumes and fit the curves $E(V)$ of the calculated total energies vs volume to the Birch-

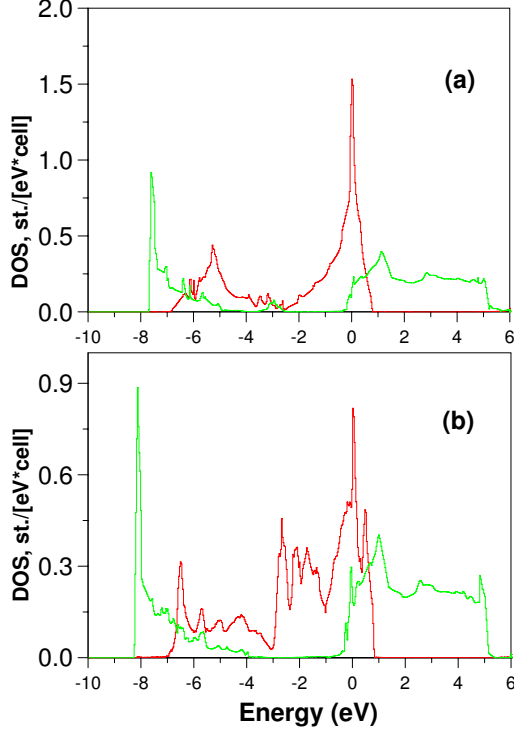


FIG. 1: (Color online). Partial density of states (DOS) of the cubic BaRuO₃. Red and green curve denote the t_{2g} and e_g band, respectively. (a) is the conventional LSDA results; (b) is the constrained orbital hybridization calculations results with the $5d$ band of Ba upshifted by 9 eV.

TABLE I: The obtained equilibrium volume V_0 , bulk modulus B_0 and its pressure derivative B'_0 of SrRuO₃. Previous experimental[27] and the theoretical results[31] from VASP and SIESTA package are also listed for comparison.

	$V_0(\text{a.u.}^3)$	B_0 (GPa)	B'_0
Present LMTO	1605	190.5	4.6
Experiment[27]	1633	192	5.3
Other theory (VASP)[31]		200	4.6
Other theory (SIESTA)[31]		219	4.4

Murnaghan equation of state. The obtained equilibrium volume V_0 , bulk modulus at equilibrium B_0 , its pressure derivative B'_0 for SrRuO₃, together with the available experimental and theoretical values are summarized in Table I. Our theoretical equilibrium volume is only about 1.7% smaller than the experimental values. Such a deviation exists normally in the LSDA calculations. Our full potential calculations agree with the experiment very well, while the pseudopotential calculation[31] slightly overestimates the bulk modulus.

Perovskite ruthenate belongs to itinerant magnet, therefore one cannot estimate the interatomic exchange

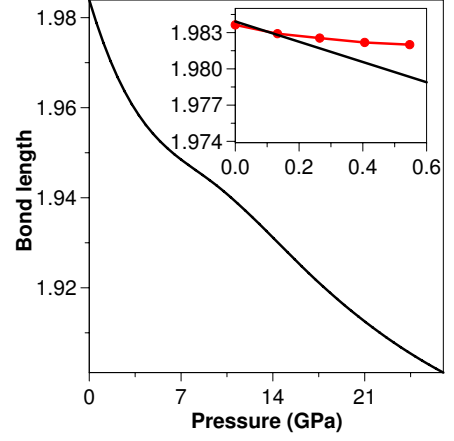


FIG. 2: (Color online). Numerical pressure dependence of the average Ru-O bond length of SrRuO₃ (in a unit of Å). The inset is a comparison between the experimental[28] (red) and numerical (black) results at low pressures.

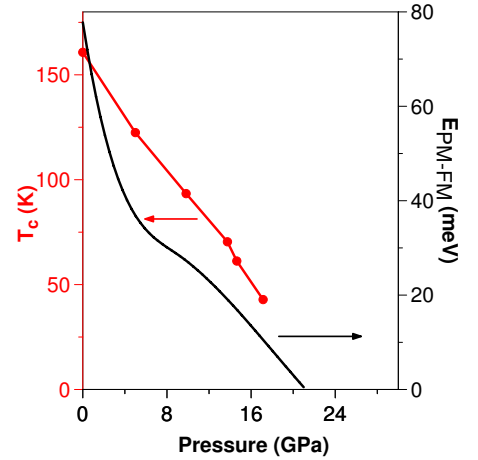


FIG. 3: (Color online). The numerical pressure dependence of the energy difference between PM and FM solution of SrRuO₃ (black), and the experimental[27] pressure dependence of the T_c (red).

interaction and T_c accurately as in the local magnet[32]. One important parameter relevant to the T_c is E_{PM-FM} , which is plotted in Fig.3. For comparison, we also plot the experimental curve of T_c vs pressure in Fig.3. It is interesting to notice that both numerical E_{PM-FM} and experimental T_c decrease monotonically and rapidly. Theoretical work predicts that the critical pressure (P_c) for FM to PM transition is about 21 GPa, after this pressure E_{PM-FM} starts to equal or less than zero. The experimental T_c at the pressures above 18 GPa is not available, but an extrapolation of the experimental data at low pressures yields a crude approximation of 23 GPa, which is quite close to our numerical results.

In summary, we introduce a method to identify the effect of covalence for a particular material by applying orbitally dependent external potential. This approach allows us to control the hybridization between the orbitals directly. Our constrained orbital hybridization calculation unambiguously identify that the covalency between the A-site cation and O ion will modify the Ru-O hybridization, consequently affect the magnetic properties significantly. We also study the effect of pressure and find that hydrostatic pressure has a small effect on the Ru-O-Ru bond angle of SrRuO_3 , while it will decrease the Ru-O length, increase the band width and result in the monotonic decrease of the magnetic ordering temperature.

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